

# **Exhibit A**

(Part 2)

SHEET 1 OF 1

<b>INFORMATION DISCLOSURE CITATION</b>  PTO-1449				ATTY. DOCKET NO. A-67824/AJT		SERIAL NO. NEW	
				APPLICANT TANG ET AL.			
				FILING DATE Herewith		GROUP not assigned	
<b>U.S. PATENT DOCUMENTS</b>							
EXAMINER'S INITIALS	PATENT NO.	DATE	NAME	CLASS	SUBCLASSES	FILING DATE	
	4,963,736	10/16/90	Douglas et al.	250	292	11/15/89	
	5,157,260	10/20/92	Mylichreest et al	250	423 R	05/17/91	
	5,179,278	01/12/93	Douglas	250	290	08/23/91	
	5,432,343	07/11/95	Gulcicek et al.	250	288	06/03/93	
	5,652,427	07/29/97	Whitehouse et al.	250	288	05/14/96	
	5,811,800	09/22/98	Franzen et al.	250	288	09/13/96	
	5,852,294	12/22/98	Gulcicek et al.	250	292	07/03/97	
<b>OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)</b>							
	Yost, R.A. and Enke, C.G., "Triple Quadrupole Mass Spectrometry for Direct Mixture Analysis and Structure Elucidation". <i>Analytical Chemistry</i> , Vol. 51, No. 12 (October 1979) p. 1251, 1252, 1256 and even pages through 1264.						
	Dawson, P.H. and Fulford, J.E. "The Effective Containment of Parent Ions and Daughter Ions in Triple Quadrupoles Used for Collisional Dissociation". <i>Int. Journal of Mass Spectrometry and Ion Physics</i> , 42 (1982) 195-211.						
	Teloy, E. and Gerlich, D., "Integral Cross Sections for Ion-Molecule Reactions. 1. The Guided Beam Technique". <i>Chemical Physics</i> 4 (1974) 417-427.						
	Jarrold, Martin F. et al., "A crossed beam study of the reaction of CO <sup>+</sup> with O <sub>2</sub> ". <i>Molecular Physics</i> (1980) Vol. 39, No. 4, 787-798.						
	McIver, Jr., Robert, et al., "Coupling a Quadrupole Mass Spectrometer and a Fourier Transform Mass Spectrometer". <i>Int. J. Mass Spectrometry and Ion Processes</i> , 64 (1985) 67-77.						
	Hagg, Conny and Szabo, Imre, "New Ion-Optical Devices Utilizing Oscillatory Electric Fields. IV. Computer Simulations of the Transport of an Ion Beam Through an Ideal Quadrupole, Hexapole, and Octopole Operating in the RF-Only Mode". <i>Int. J. Mass Spectrometry and Ion Processes</i> , 73 (1986) 295-312.						
	Smith, Richard D., et al., "Capillary Zone Electrophoresis - Mass Spectrometry Using an Electrospray Ionization Interface". <i>Anal. Chem.</i> (1988) 60, 436-441.						
Beu, Steven C., et al., "Fourier-Transform Electrospray Instrumentation for Tandem High-Resolution Mass Spectrometry of Large Molecules". <i>Am. Soc. for Mass Spectrometry</i> (1993) 1044-0305.							
EXAMINER			DATE CONSIDERED				
			12/15/10				

EXAMINER. Initial if reference considered, whether or not citation is in conformance with MPEP 609; draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

139247 1449A FRM (8/96)

TA 34

T005802

## PTO - 1449 CHECKLIST

Serial No. 09/454273  
Examiner: 3keels  
Date to Examiner: 6/27/00

For each considered document, both the month and year **MUST** be provided - no exceptions. Class and subclass data **MUST** either be provided or the space lined through. The Examiners name and the date the disclosure citation was considered **MUST** be provided at the bottom of the PTO 1449.

### CHECK OFF THE FOLLOWING ITEMS AS COMPLETED

For each citation considered:

1. ☐ Initials inserted in left-hand column for each citation considered
2. ☐ Month ☐ Year - inserted in appropriate box (if unavailable, citation is incomplete - go to item 4)
3. ☐ Class ☐ Subclass - inserted in appropriate box (if unavailable, citation is still proper, but you **MUST** draw a line through each blank space)

For each citation not considered or incomplete:

4. ☐ Citation lined through if not considered or incomplete

At bottom of PTO 1449:

5. ☐ Examiner's name in appropriate place
6. ☐ Enter the date citations were considered in the appropriate place

## File History Report

☒ Paper number 3 is missing from the United States Patent and Trademark Office's original copy of the file history. No additional information is available.

☐ The following page(s) \_\_\_\_\_ of paper number \_\_\_\_\_ is/are missing from the United States Patent and Trademark Office's original copy of the file history. No additional information is available

Additional comments: \_\_\_\_\_



**UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office**

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
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09/154,273 12/13/95 TANG

K A-6782, 1611

ALDO J. TEST  
FLEHR HOHBACH TEST  
ALBRITTON & HERBERT LLP  
SUITE 3400 FOUR EMBARCADERO CENTER  
SAN FRANCISCO CA 94111

MM91/1206

EXAMINER
----------

SMITH, J	
ART UNIT	PAPER NUMBER

2381  
DATE MAILED:

12/06/00

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

<b>Office Action Summary</b>	Application No. 09/454,273		Applicant(s) TANG ET AL.	
	Examiner Johnnie L Smith II		Art Unit 2881	

- The MAILING DATE of this communication appears on the cover sheet with the correspondence address -

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136 (a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133).
- Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

1) ☐ Responsive to communication(s) filed on \_\_\_\_\_

2a) ☐ This action is FINAL                      2b) ☒ This action is non-final.

3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

4) ☐ Claim(s) \_\_\_\_\_ is/are pending in the application.

4a) Of the above claim(s) \_\_\_\_\_ is/are withdrawn from consideration.

5) ☐ Claim(s) \_\_\_\_\_ is/are allowed.

6) ☒ Claim(s) 1-8 is/are rejected.

7) ☐ Claim(s) \_\_\_\_\_ is/are objected to.

8) ☐ Claims \_\_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

9) ☐ The specification is objected to by the Examiner.

10) ☒ The drawing(s) filed on 03 December 1999 is/are objected to by the Examiner.

11) ☐ The proposed drawing correction filed on \_\_\_\_\_ is: a) ☐ approved b) ☐ disapproved.

12) ☐ The oath or declaration is objected to by the Examiner.

**Priority under 35 U.S.C. § 119**

13) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

a) ☐ All   b) ☐ Some \*   c) ☐ None of.

1 ☐ Certified copies of the priority documents have been received.

2 ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_\_

3 ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

\* See the attached detailed Office action for a list of the certified copies not received.

14) ☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. & 119(e).

**Attachment(s)**

15) ☒ Notice of References Cited (PTO-892)

16) ☒ Notice of Draftsperson's Patent Drawing Review (PTO-948)

17) ☒ Information Disclosure Statement(s) (PTO-1449) Paper No(s) 2

18) ☐ Interview Summary (PTO-413) Paper No(s). \_\_\_\_\_

19) ☐ Notice of Informal Patent Application (PTO-152)

20) ☐ Other \_\_\_\_\_

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## DETAILED ACTION

### *Drawings*

1. This application has been filed with informal drawings, which are acceptable for examination purposes only. Formal drawings will be required when the application is allowed.

### *Claim Rejections - 35 USC § 112*

2. The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter, which the applicant regards as his invention.

3. Claim 2 is rejected under 35 U.S.C. 112, second paragraph, as being incomplete for omitting essential steps, such omission amounting to a gap between the steps. See MPEP § 2172.01. The omitted steps are: The steps needed for mass ions to be produced at atmospheric pressure where in adducts ions would be formed, and introduced into a mass analyzer. In it's current state the claim would be rendered indefinite.

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*Claim Rejections - 35 USC § 102*

4. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States

5. Claims 1, 3, and 4 are rejected under 35 U.S.C. 102(b) as being anticipated by Whitehouse et al. In reference to claim 1 and 4, Whitehouse et al discloses a mass spectrometer system including a mass analyzer disposed in a high vacuum chamber for analyzing ions formed at or near atmospheric pressure and directed to the analyzer through intermediate vacuum chambers including two evacuating chambers ion guides in both of said chambers, an interchamber ion lens and a DC voltage source connected to said interchamber lens (column 7 line 51 through column 8 line 41). In reference to claim 3, the method of operating a mass spectrometer system including a mass analyzer that analyzes ions formed at atmospheric pressure. The said system including a first and second multipole ion guides, and the step of applying a DC voltage between the ion lens and second multipole ion guide, Whitehouse discloses such a method in column 7 line 7 through column 8 line 26, and column 9 lines 18 through 42).



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*Claim Rejections - 35 USC § 103*

6. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

7. The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

8. Claims 5 through 8 are rejected under 35 U.S.C. 103(a) as being unpatentable over Whitehouse et al. Whitehouse does not give the exact numerals claimed by applicant in the above mentioned claims, but does discuss the differentiation and usage attached there with involving pressure within the

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chamber and the offset voltage (column 10 line 36 through column 11 line 40). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the method of Whitehouse for the purposes of establishing a stable trajectory entering and leaving the multipole ion guides.

### *Conclusion*

9. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure. The following references are placed herein for record purposes. The references contain art relevant to the art being introduced within this application. US 6107623 (Bateman et al) august 2000, US 6015972 (Hager) January 2000, and US 5432343 (Gulcicek et al) July 1995. These patents contain ion guides, mass analyzers, and lens.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Johnnie L Smith II whose telephone number is 703-305-0380. The examiner can normally be reached on M-F 7-3:30.

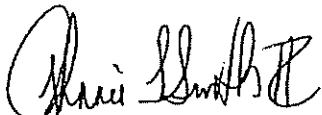
If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Teresa Arroyo can be reached on 703-308-4782. The fax phone numbers for the organization where this application or proceeding is

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assigned are 703-308-7722 for regular communications and for After Final communications.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 703-308-0956.



Johnnie L. Smith II  
December 4, 2000



TERESA M. ARROYO  
SUPERVISORY PATENT EXAMINER  
TECHNOLOGY CENTER 2800

<b>Notice of References Cited</b>				Application/Control No.		Applicant(s)/Patent Under Reexamination			
				09/454,273		TANG ET AL			
				Examiner		Art Unit			
				Johnnie L. Smith II		2881			
						Page 1 of 1			
<b>U.S. PATENT DOCUMENTS</b>									
*		DOCUMENT NO	DATE	NAME	CLASS	SUBCLASS	DOCUMENT SOURCE **		
							APS	OTHER	
<input type="checkbox"/>	A	us005652427a	Jul. 1997	Whitehouse et al	250	288	<input type="checkbox"/>	<input type="checkbox"/>	
<input type="checkbox"/>	B	us005432343a	Jul. 1995	Gulclcek	250	288	<input type="checkbox"/>	<input type="checkbox"/>	
<input type="checkbox"/>	C	us006107623a	Aug. 2000	Bateman et al	250	282	<input type="checkbox"/>	<input type="checkbox"/>	
<input type="checkbox"/>	D	us006015972a	Jan. 2000	Hager	250	282	<input type="checkbox"/>	<input type="checkbox"/>	
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<b>FOREIGN PATENT DOCUMENTS</b>									
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<b>NON-PATENT DOCUMENTS</b>									
*		DOCUMENT (Including Author, Title Date, Source, and Pertinent Pages)						DOCUMENT SOURCE **	
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<input type="checkbox"/>	X							<input type="checkbox"/>	<input type="checkbox"/>

\*A copy of this reference is not being furnished with this Office action. (See Manual of Patent Examining Procedure, Section 707.05(a))  
 \*\*APS encompasses any electronic search i.e. text, image, and Commercial Databases  
 U.S. Patent and Trademark Office  
 PTO-892 (Rev. 03-98)

Part

T005812

Form PTO 948 (Rev. 8-98)

U.S. DEPARTMENT OF COMMERCE Patent and Trademark Office

Application No.

9/454212

NOTICE OF DRAFTSPERSON'S  
PATENT DRAWING REVIEWThe drawing(s) filed (insert date) 12/3/99A. ☐ approved by the Draftsperson under 37 CFR 1.84 or 1.152.B. ☒ objected to by the Draftsperson under 37 CFR 1.84 or 1.152 for the reasons indicated below. The Examiner will require submission of new, corrected drawings when necessary. Corrected drawing must be submitted according to the instructions on the back of this notice.

<p>1. DRAWINGS 37 CFR 1.84(a): Acceptable categories of drawings: Black ink. Color. Color drawings are not acceptable until petition is granted. Fig(s) _____ Pencil and non black ink not permitted. Fig(s) _____</p> <p>2. PHOTOGRAPHS 37 CFR 1.84(b) 1 full-tone set is required. Fig(s) _____ Photographs not properly mounted (must use Bristol board or photographic double-weight paper). Fig(s) _____ Poor quality (half-tone). Fig(s) _____</p> <p>3. TYPE OF PAPER 37 CFR 1.84(c) Paper not flexible, strong, white, and durable. Fig(s) _____ Erasures, alterations, overwritings, interlineations, folds, copy machine marks not accepted. Fig(s) _____ Mylar, vellum paper is not acceptable (too thin). Fig(s) _____</p> <p>4. SIZE OF PAPER 37 CFR 1.84(f): Acceptable sizes: 21.0 cm by 29.7 cm (DIN size A4) 21.6 cm by 27.9 cm (B 1/2 x 11 inches) All drawing sheets not the same size Sheet(s) _____ Drawings sheets not an acceptable size. Fig(s) _____</p> <p>5. MARGINS 37 CFR 1.84(g): Acceptable margins: Top 2.5 cm Left 2.5 cm Right 1.5 cm Bottom 1.0 cm SIZE: A4 Size Top 2.5 cm Left 2.5 cm Right 1.5 cm Bottom 1.0 cm SIZE: 8 1/2 x 11 Margins not acceptable. Fig(s) <u>1, 3A, 13B</u> Top (T) _____ Left (L) _____ Right (R) _____ Bottom (B) _____</p> <p>6. VIEWS 37 CFR 1.84(h) REMINDER: Specification may require revision to correspond to drawing changes. Partial views 37 CFR 1.84(h)(2) Brackets needed to show figure as one entity. Fig(s) _____ Views not labeled separately or properly. Fig(s) _____ Enlarged view not labeled separately or properly. Fig(s) _____</p> <p>7. SECTIONAL VIEWS 37 CFR 1.84(h)(3) Hatching not indicated for sectional portions of an object. Fig(s) _____ Sectional designation should be noted with Arabic or Roman numbers Fig(s) _____</p>	<p>8. ARRANGEMENT OF VIEWS 37 CFR 1.84(i) Words do not appear on a horizontal, left-to-right fashion when page is either upright or turned so that the top becomes the right side, except for graphs. Fig(s) _____</p> <p>9. SCALE 37 CFR 1.84(k) Scale not large enough to show mechanism without crowding when drawing is reduced in size to two-thirds in reproduction. Fig(s) _____</p> <p>10. CHARACTER OF LINES, NUMBERS, &amp; LETTERS 37 CFR 1.84(l) Lines, numbers &amp; letters not uniformly thick and well defined, clean, durable, and black (poor line quality). Fig(s) <u>1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100</u></p> <p>11. SHADING 37 CFR 1.84(m) Solid black areas pale. Fig(s) _____ Solid black shading not permitted. Fig(s) _____ Shade lines, pale, rough and blurred. Fig(s) _____</p> <p>12. NUMBERS, LETTERS, &amp; REFERENCE CHARACTERS 37 CFR 1.84(n) Numbers and reference characters not plain and legible. Fig(s) <u>1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100</u> Figure legends are poor. Fig(s) _____ Numbers and reference characters not oriented in the same direction as the view. 37 CFR 1.84(p)(1) Fig(s) _____ English alphabet not used. 37 CFR 1.84(p)(2) Fig(s) _____ Numbers, letters, and reference characters must be at least .32 cm (1/8 inch) high. 37 CFR 1.84(p)(3) Fig(s) <u>1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100</u></p> <p>13. LEAD LINES 37 CFR 1.84(q) Lead lines cross each other. Fig(s) _____ Lead lines missing. Fig(s) _____</p> <p>14. NUMBERING OF SHEETS OF DRAWINGS 37 CFR 1.84(i) Sheets not numbered consecutively, and in Arabic numerals beginning with number 1. Sheet(s) _____</p> <p>15. NUMBERING OF VIEWS 37 CFR 1.84(u) Views not numbered consecutively, and in Arabic numerals beginning with number 1. Fig(s) _____</p> <p>16. CORRECTIONS 37 CFR 1.84(w) Corrections not made from prior PTO-948 dated _____</p> <p>17. DESIGN DRAWINGS 37 CFR 1.152 Surface shading shown not appropriate. Fig(s) _____ Solid black shading not used for color contrast. Fig(s) _____</p>
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COMMENTS

REVIEWER

DATE

TELEPHONE NO.

ATTACHMENT TO PAPER NO.

TA 45

T005813

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

TANG et al.

Serial No. 09/454,273

Filed: December 3, 1999

For: *MASS SPECTROMETER SYSTEM  
INCLUDING A DOUBLE ION GUIDE  
INTERFACE AND METHOD OF  
OPERATION*



Examiner: Smith II, J.  
Art Unit: 2881

SUBMISSION OF  
FORMAL DRAWINGS

Date: January 12, 2001

**CERTIFICATE OF MAILING (37 CFR 1.8(A))**

I hereby certify that this paper (along with any referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as First Class Mail in an envelope addressed to: Attn: Official Draftsman, Assistant Commissioner for Patents, Washington, D.C. 20231 on January 12, 2001.

Signed:

*Kathryn Marley*  
Kathryn Marley

**Attn: Official Draftsman**  
Assistant Commissioner for Patents  
Washington, D. C. 20231

Sir:

Enclosed for the referenced file are eight (8) sheets of formal drawings consisting of Figures 1-8 which are being filed to replace the informal drawings filed with the application.

The Commissioner is authorized to charge any fee associated with the filing of the enclosed formal drawings (or credit any overpayment thereof) to Deposit Account No. 06-1300 (Order No. A-67824/AJT).

Respectfully submitted,

*Aldo J. Test*  
Aldo J. Test, Reg. No. 18,048

FLEHR HOHBACH TEST ALBRITTON & HERBERT LLP  
Suite 3400, 4 Embarcadero Center  
San Francisco, CA 94111-4187  
Tel. (650) 494-8700

A-67824/AJT

TA 46

(1023367)

T005814

2881

#5  
Lrrw/dwgs  
J. McMillan  
1/15/01

TC 2001-01-12-001

RECEIVED

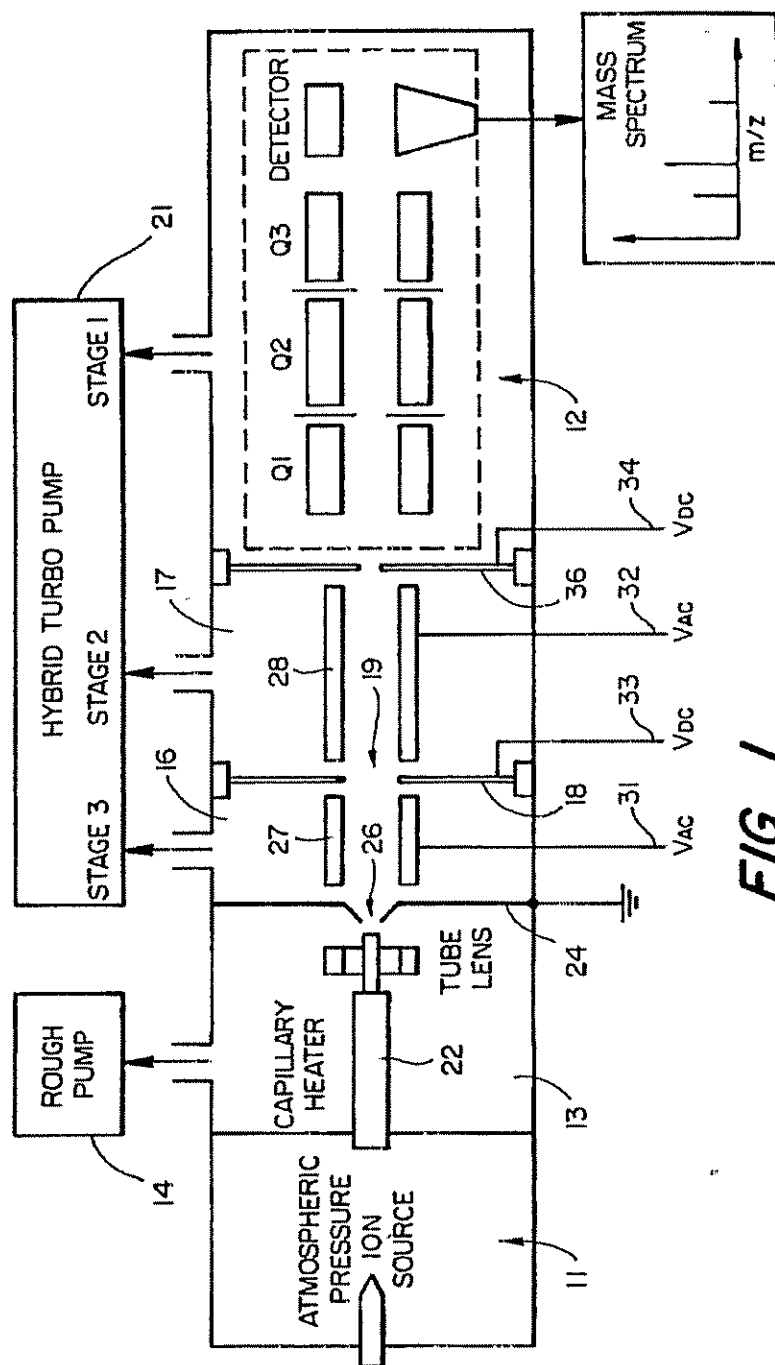
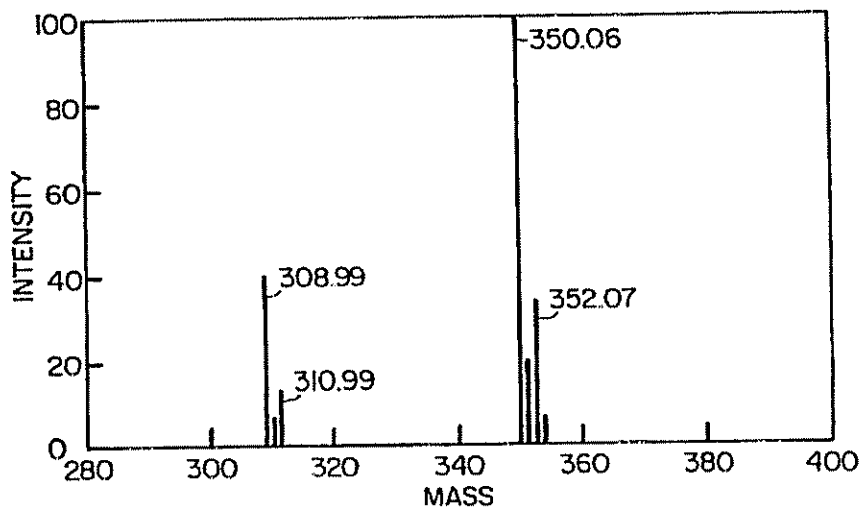


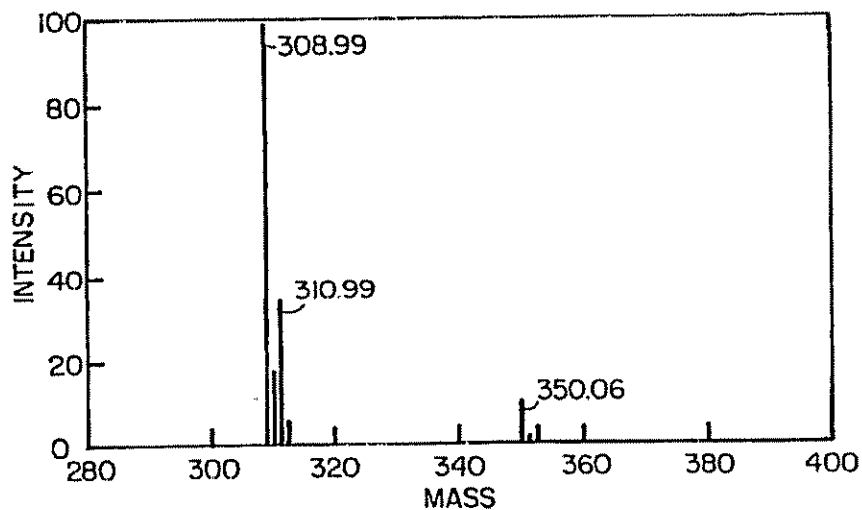
FIG. 1

1/8

2/8



**FIG\_2A**



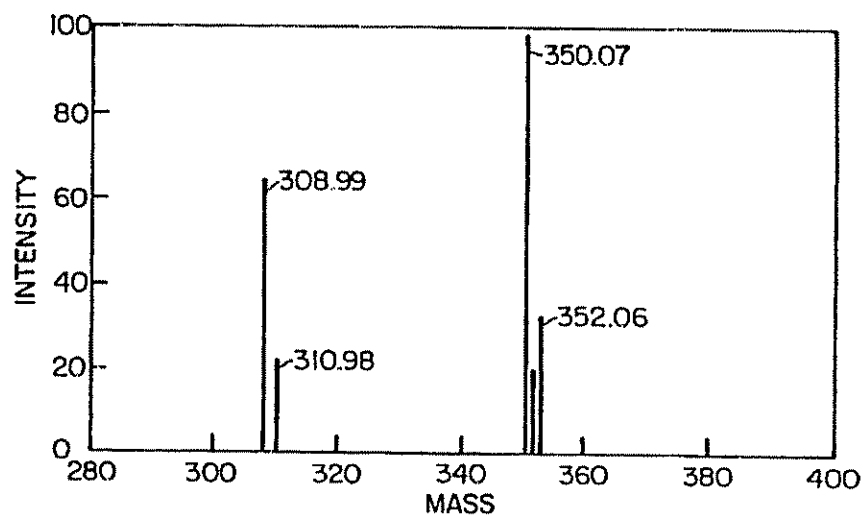
**FIG\_2B**

TA 48

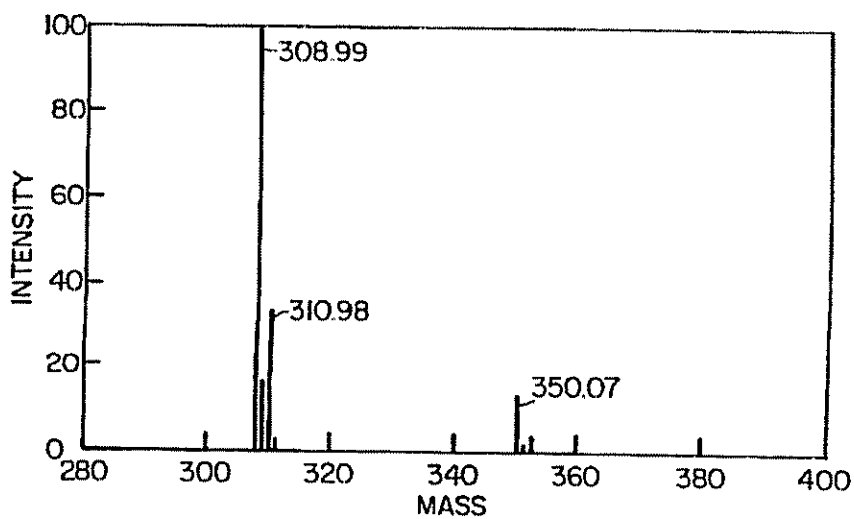
T005816



3/8



**FIG\_3A**

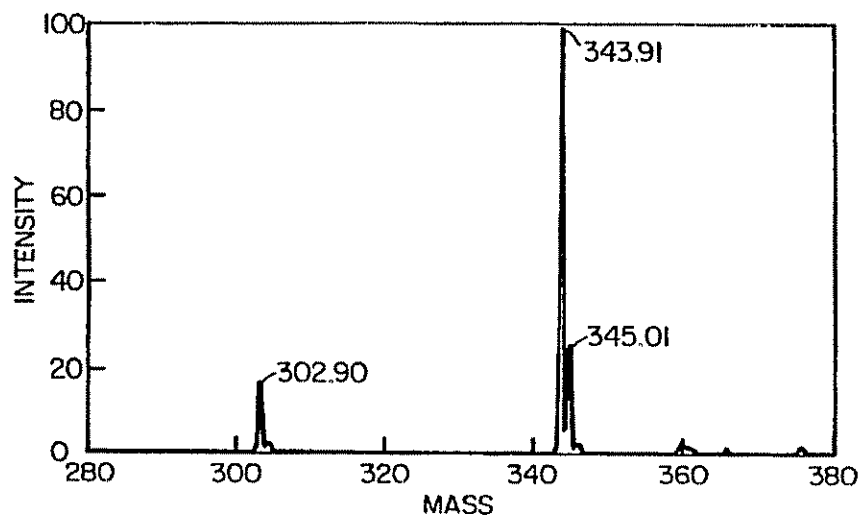


**FIG\_3B**

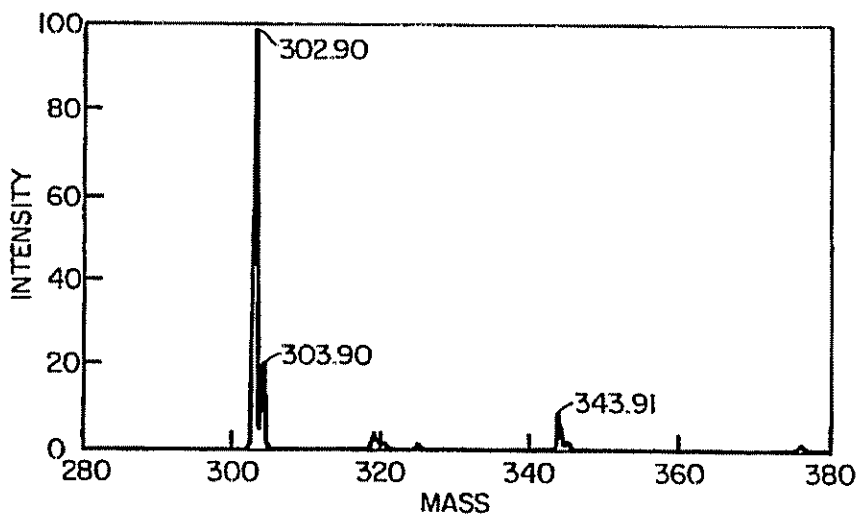
TA 49

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4/8

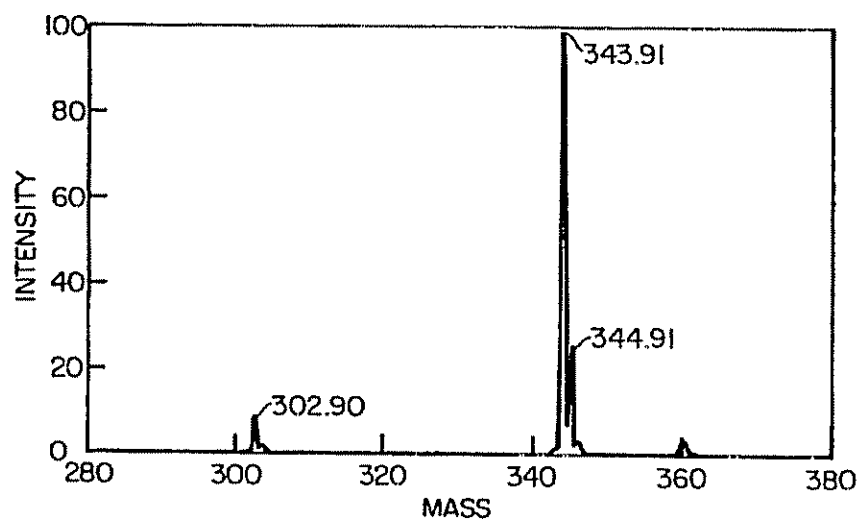


**FIG\_4A**

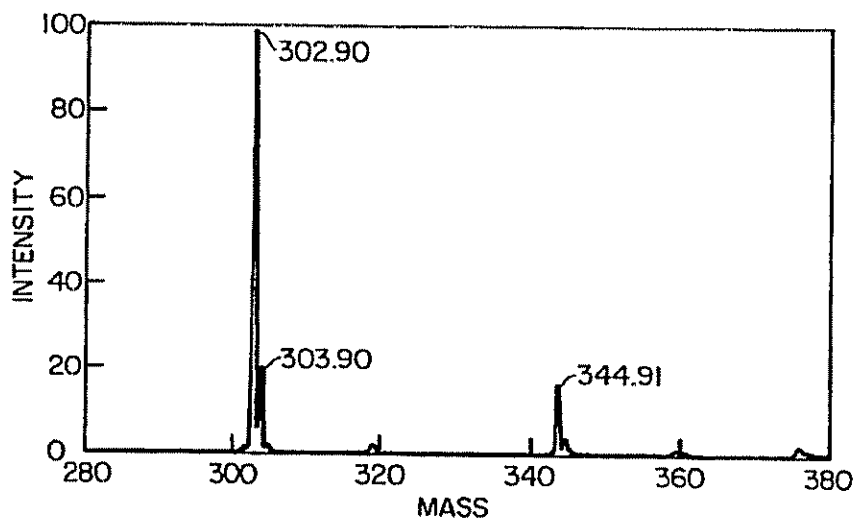


**FIG\_4B**

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**FIG\_5A**

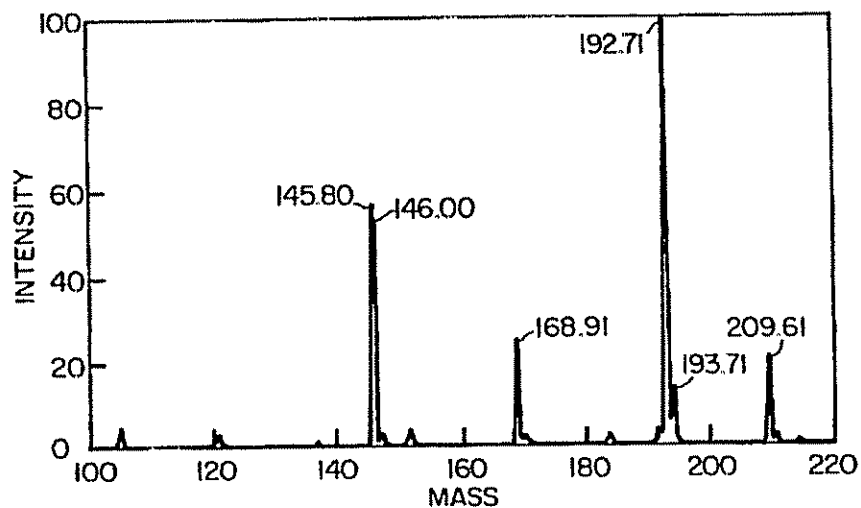


**FIG\_5B**

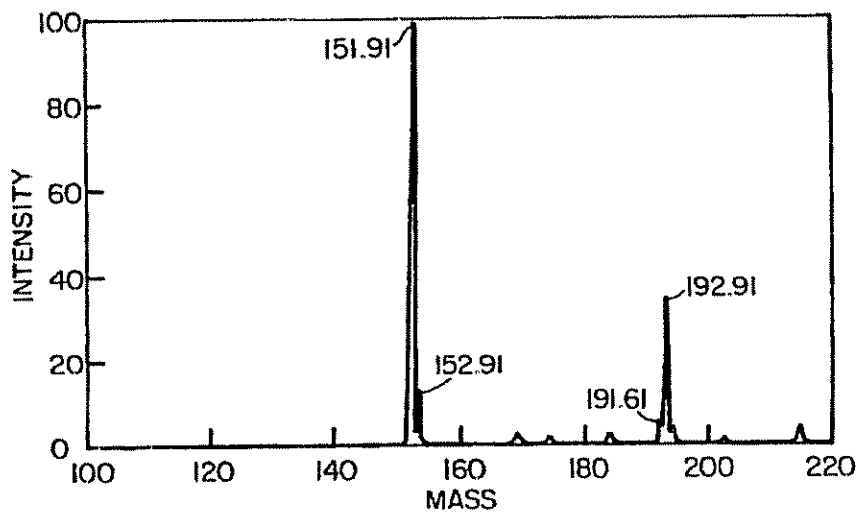
TA 51

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**FIG\_6A**

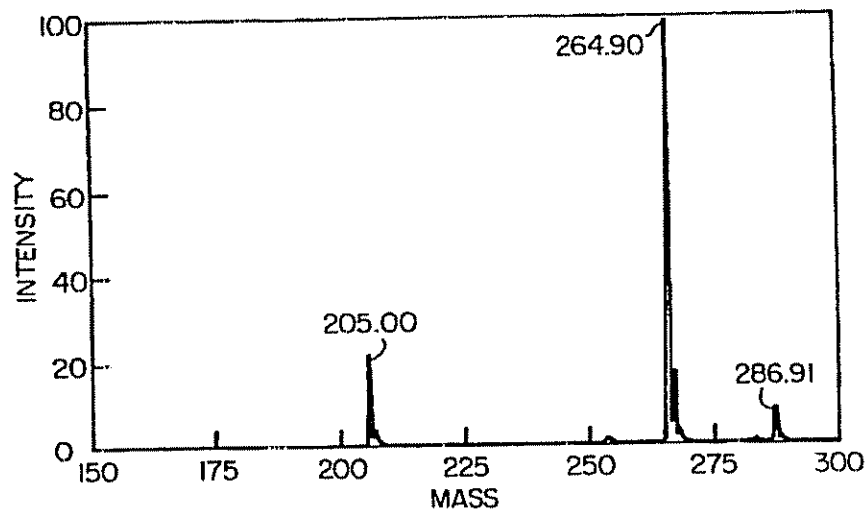


**FIG\_6B**

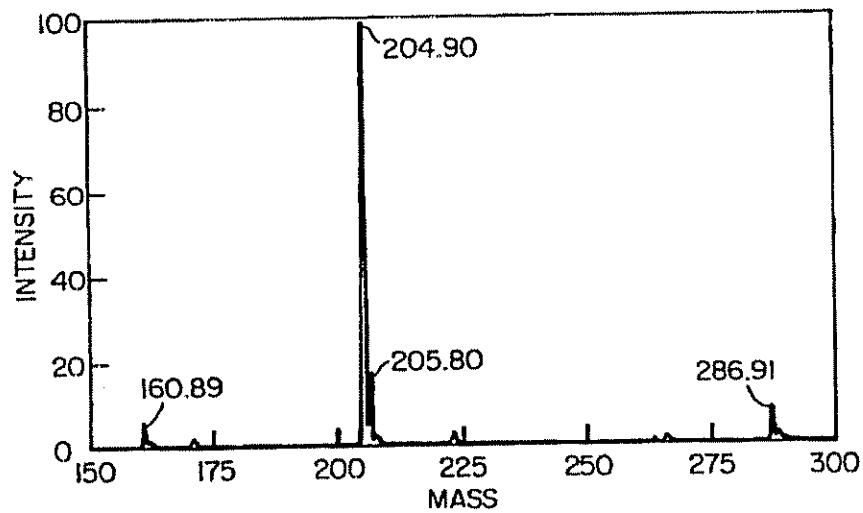
TA 52

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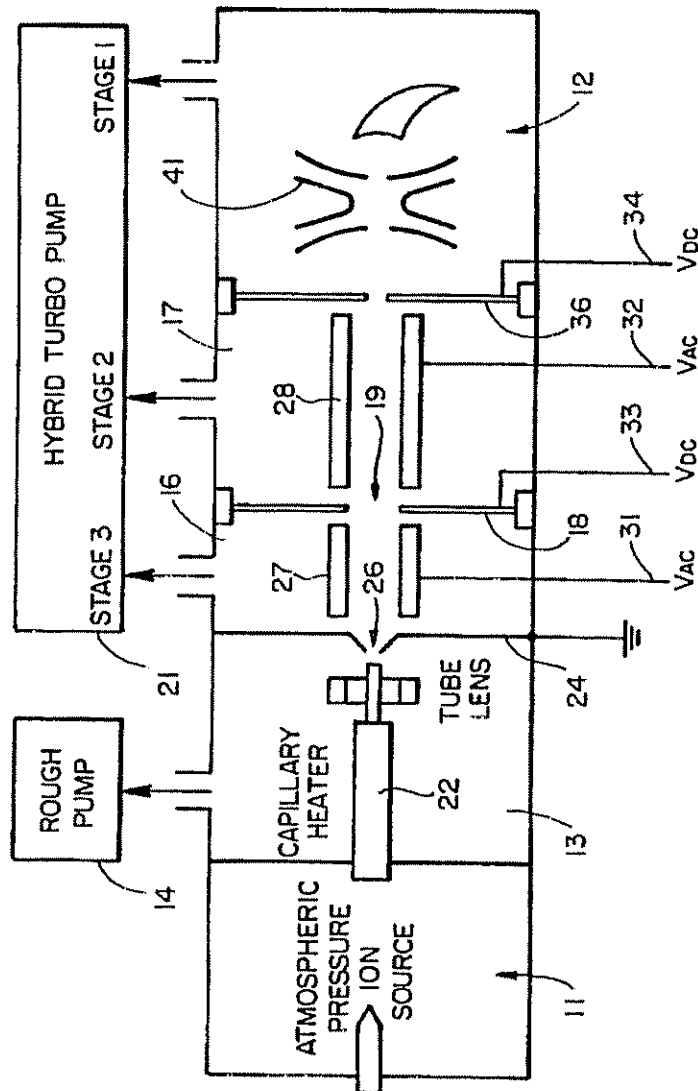
**FIG\_7A**



**FIG\_7B**

TA 53

T005821



**FIG-8**

TA 54

T005822


**UNITED STATES DEPARTMENT OF COMMERCE**  
**United States Patent and Trademark Office**

 Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
 Washington, D.C. 20231

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
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09/454,270 12/03/94 TANG

I. A-6/824/AJT

EXAMINER

MMC2/0628

 ALDO J TEST  
 FLEHR HOHBACH TEST  
 ALBRITTON & HERBERT LLP  
 SUITE 3400 FOUR EMBARADERO CENTER  
 SAN FRANCISCO CA 94111

SMITH, J

ART UNIT

PAPER NUMBER

2981

DATE MAILED:

06/28/01

Please find below and/or attached an Office communication concerning this application or proceeding.


Commissioner of Patents and Trademarks

<b>Notice of Abandonment</b>	Application No.	Applicant(s)	
	09/454,273	TANG ET AL.	
	Examiner	Art Unit	
	Johnnie L Smith II	2881	

— The MAILING DATE of this communication appears on the cover sheet with the correspondence address—

This application is abandoned in view of:

- ☒ Applicant's failure to timely file a proper reply to the Office letter mailed on 06 December 2000.
  - ☐ A reply was received on \_\_\_\_\_ (with a Certificate of Mailing or Transmission dated \_\_\_\_\_), which is after the expiration of the period for reply (including a total extension of time of \_\_\_\_\_ month(s)) which expired on \_\_\_\_\_.
  - ☐ A proposed reply was received on \_\_\_\_\_, but it does not constitute a proper reply under 37 CFR 1.113 (a) to the final rejection (A proper reply under 37 CFR 1.113 to a final rejection consists only of: (1) a timely filed amendment which places the application in condition for allowance; (2) a timely filed Notice of Appeal (with appeal fee); or (3) a timely filed Request for Continued Examination (RCE) in compliance with 37 CFR 1.114).
  - ☒ No reply has been received.
- ☐ Applicant's failure to timely pay the required issue fee and publication fee, if applicable, within the statutory period of three months from the mailing date of the Notice of Allowance (PTOL-85).
  - ☐ The issue fee and publication fee, if applicable, was received on \_\_\_\_\_ (with a Certificate of Mailing or Transmission dated \_\_\_\_\_), which is after the expiration of the statutory period for payment of the issue fee (and publication fee) set in the Notice of Allowance.
  - ☐ The submitted fee of \$\_\_\_\_\_ is insufficient. A balance of \$\_\_\_\_\_ is due.  
The issue fee required by 37 CFR 1.18 is \$\_\_\_\_\_. The publication fee, if required by 37 CFR 1.18(d), is \$\_\_\_\_\_.
  - ☐ The issue fee and publication fee, if applicable, has not been received.
- ☐ Applicant's failure to timely file new formal drawings as required by, and within the three-month period set in, the Notice of Allowability (PTO-37).
  - ☐ Proposed new formal drawings were received on \_\_\_\_\_ (with a Certificate of Mailing or Transmission dated \_\_\_\_\_), which is after the expiration of the period for reply.
  - ☐ The proposed new formal drawings filed on \_\_\_\_\_ are not acceptable and the period for reply has expired.
  - ☐ No proposed new formal drawings have been received.
- ☐ The letter of express abandonment which is signed by the attorney or agent of record, the assignee of the entire interest, or all of the applicants
- ☐ The letter of express abandonment which is signed by an attorney or agent (acting in a representative capacity under 37 CFR 1.34(a)) upon the filing of a continuing application
- ☐ The decision by the Board of Patent Appeals and Interference rendered on \_\_\_\_\_ and because the period for seeking court review of the decision has expired and there are no allowed claims
- ☐ The reason(s) below:

  
**JACK BERMAN**  
 PRIMARY EXAMINER



PTO/SB-38 (37-CFR)  
Approved for use through 7/5/2005. OMB 3524-0037  
U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

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<p>Bring completed form to: File Information Unit Crystal Plaza Three, Room 1D01 2021 South Clark Place Arlington, VA Telephone: (703) 308-2733</p> <p style="text-align: center; font-weight: bold;">JAN 24 2005</p>	<p>In re Application of _____</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%;">Application Number <b>09/454,273</b></td> <td style="width: 50%;">Filed <b>12-3-97</b></td> </tr> </table> <p style="text-align: right;">Paper No. <b>7</b></p>	Application Number <b>09/454,273</b>	Filed <b>12-3-97</b>
Application Number <b>09/454,273</b>	Filed <b>12-3-97</b>		

I hereby request access under 37 CFR 1.14(a)(1)(iv) to the application file record of the above-identified ABANDONED application, which is identified in, or to which a benefit is claimed, in the following document (as shown in the attachment):

United States Patent Application Publication No. \_\_\_\_\_, page, \_\_\_\_\_ line \_\_\_\_\_

United States Patent Number **6,528,784**, column \_\_\_\_\_, line, \_\_\_\_\_ or \_\_\_\_\_

WIPO Pub. No. \_\_\_\_\_, page \_\_\_\_\_, line \_\_\_\_\_

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         the pending application as originally filed; or  
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<p>_____ Signature</p> <p>_____ Typed or printed name</p> <p>_____ Registration Number, if applicable</p> <p>_____ Telephone Number</p>	<p style="text-align: center;">_____ Date</p> <div style="border: 1px solid black; padding: 5px; margin-top: 10px;"> <p style="text-align: center; font-weight: bold;">FOR PTO USE ONLY</p> <p>Approved by _____ (initials)</p> <p>Unit _____</p> </div>
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T005825

PATENT APPLICATION FEE DETERMINATION RECORD Effective November 10, 1998					Application or Docket Number <span style="font-size: 1.2em;">09/454223</span>																																																								
<div style="display: flex; justify-content: space-between;"> <div style="width: 60%;"> <p><b>CLAIMS AS FILED - PART I</b></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 20%;">FOR</th> <th style="width: 20%;">NUMBER FILED (Column 1)</th> <th style="width: 20%;">NUMBER EXTRA (Column 2)</th> <th style="width: 20%;"></th> <th style="width: 20%;"></th> </tr> </thead> <tbody> <tr> <td>BASIC FEE</td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>TOTAL CLAIMS</td> <td style="text-align: center;">9</td> <td>minus 20=</td> <td style="text-align: center;">*</td> <td style="text-align: center;">0</td> </tr> <tr> <td>INDEPENDENT CLAIMS</td> <td style="text-align: center;">4</td> <td>minus 3=</td> <td style="text-align: center;">*</td> <td style="text-align: center;">1</td> </tr> <tr> <td colspan="5">MULTIPLE DEPENDENT CLAIM PRESENT <span style="float: right;">Y</span></td> </tr> </tbody> </table> <p><small>* If the difference in column 1 is less than zero, enter "0" in column 2</small></p> </div> <div style="width: 35%;"> <p><b>SMALL ENTITY TYPE</b> <input type="checkbox"/> OR <b>OTHER THAN SMALL ENTITY</b></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 20%;">RATE</th> <th style="width: 20%;">FEE</th> <th style="width: 20%;"></th> <th style="width: 20%;">RATE</th> <th style="width: 20%;">FEE</th> </tr> </thead> <tbody> <tr> <td></td> <td style="text-align: center;">380.00</td> <td>OR</td> <td></td> <td style="text-align: center;">760.00</td> </tr> <tr> <td>X\$ 9=</td> <td></td> <td>OR</td> <td>X\$18=</td> <td></td> </tr> <tr> <td>X39=</td> <td></td> <td>OR</td> <td>X78=</td> <td style="text-align: center;">78</td> </tr> <tr> <td>+130=</td> <td></td> <td>OR</td> <td>+260=</td> <td style="text-align: center;">260</td> </tr> <tr> <td>TOTAL</td> <td></td> <td>OR</td> <td>TOTAL</td> <td style="text-align: center;">1098</td> </tr> </tbody> </table> </div> </div>							FOR	NUMBER FILED (Column 1)	NUMBER EXTRA (Column 2)			BASIC FEE					TOTAL CLAIMS	9	minus 20=	*	0	INDEPENDENT CLAIMS	4	minus 3=	*	1	MULTIPLE DEPENDENT CLAIM PRESENT <span style="float: right;">Y</span>					RATE	FEE		RATE	FEE		380.00	OR		760.00	X\$ 9=		OR	X\$18=		X39=		OR	X78=	78	+130=		OR	+260=	260	TOTAL		OR	TOTAL	1098
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<p><small>* If the entry in column 1 is less than the entry in column 2, write "0" in column 3</small></p> <p><small>** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20."</small></p> <p><small>*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3."</small></p> <p><small>The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1</small></p>																																																													

Molecular Physics, 1980, Vol. 39, No. 4, 787-798

# A crossed beam study of the reaction of $\text{CU}^-$ with $\text{O}_2$

by MARTIN F. JARROLD, KEITH BIRKINSHAW†  
and DAVID M. HIRST

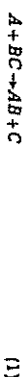
Department of Chemistry and Molecular Science,  
University of Warwick, Coventry CV4 7AL, England

(Received 23 August 1979)

A new crossed beam instrument for the investigation of ion-molecule reactions is described. The reaction  $\text{CO}^+ + \text{O}_2 \rightarrow \text{CO}_2^+ + \text{O}$  has been studied over the range of initial relative translational energies from 1.6 to 10 eV. The cross-section increases as the energy is raised to 5 eV and then decreases as the energy is increased further. The reaction proceeds by a direct mechanism at all energies, though at low energies there are substantial inter-  
actions between all four atoms. As the initial energy is raised the mechanism becomes more impulsive and there is evidence for the formation of products in an excited electronic state.

## 1. INTRODUCTION

A wide variety of ion-molecule reactions has been investigated by the molecular beam method [1, 2] but, with the exception of reactions of the type

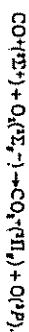


the majority are hydrogen abstraction or proton transfer reactions. Here we present the results of a crossed molecular beam study of the reaction



in the range of relative kinetic energies from 1.6 eV to 10 eV.

It is known from flowing afterglow [3-5] and SIFT studies that at thermal energy the reaction between  $\text{CO}^+$  and  $\text{O}_2$  leads almost exclusively to  $\text{O}_2^+$  in spite of the fact that for ground state reagents, reaction (2) is exothermic by 0.58 eV [6] and is spin allowed



Energy-dependent studies by the injected ion-dipole tube method show that the cross-section for charge exchange falls from about  $20 \text{ \AA}^2$  to  $1 \text{ \AA}^2$  over the relative energy range of 0.04 to 3 eV and no other reaction was observed [7]. In contrast we find in our molecular beam experiments that reaction (2) occurs effectively in the energy range in which we are working and we believe this to be the first reported observation of reaction (2). Intensity contour diagrams of the product distribution will be presented later. In addition to  $\text{CO}_2^+$  we have

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excited  $C_1$ ,  $O^+$ , and  $O_2^+$  from  $CO^+ + O_2$  collisions and have measured the angular distributions of these ions. As discussed subsequently, it is believed that the reactant  $CO^+$  is almost all in the ground electronic state.

## 2. EXPERIMENTAL

A schematic diagram of the apparatus is shown in figure 1. The system is enclosed in a large stainless steel chamber which is pumped by a 1700 l s<sup>-1</sup> diffusion pump (Edwards 250/700 DIFSTARK). The ion source and neutral beam source chambers are each differentially pumped by a 280 l s<sup>-1</sup> diffusion pump (Edwards 100/300 DIFSTARK). Around the inside of the main chamber is a large cold shield which is maintained at liquid nitrogen temperature. The operating pressures are less than 5 × 10<sup>-4</sup> torr in the main chamber and less than 5 × 10<sup>-6</sup> torr in the neutral beam chamber.

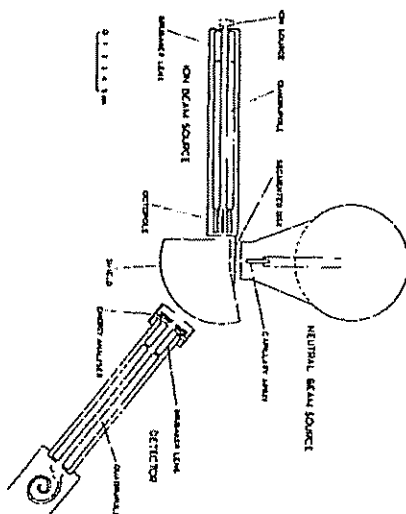


Figure 1. Schematic diagram of ion source, neutral beam source and detector.

The ion beam source has been described previously [3]. Ions are produced by electron impact in an EA1 QUD150 ionizer, mass selected by a quadrupole mass filter (QZ5<sup>+</sup> rods, VG Q8 power supply) and focused by an electrostatic focussable lens. With this system high intensity ion beams are obtained with angular spread ( $\Delta\theta_{FWHM}$ ) determined by space charge effects. The energy spread ( $\Delta E_{FWHM}$ ) in all the present experiments is given approximately by  $0.16 + 0.042E$  eV, where  $E$  is the nominal ion energy. The neutral beam source consists of a differentially pumped capillary array followed by a collimating aperture 9 mm from the source. From geometric considerations the maximum angular divergence is  $8^\circ$ .

Crossed beam study of  $\text{CO}^+ + \text{O}_2$ 

The crossing region and flight path to the detector are shielded from stray magnetic and electric fields by a shield constructed from non-magnetic stainless steel, 0.004" Tishfield and fine mesh grid. The detector can be rotated both horizontally and vertically about the crossing point by gear trains operated from outside the vacuum chamber. The detector consists of an energy analyzer, followed by a Bruchaker lens and a quadrupole mass filter (0.25" rods, EAT QUAD-250 power supply). Ions are detected at the end of the quadrupole either by a Faraday cup and an electrometer or by pulse counting with a channeltron set off-axis.

The energy analyser (figure 1) is an RPD analyser using high transparency grids. Considerable effort has been expended in producing a near ideal transmission function. The energy analyser is enclosed in a cover which is heated to 150°C to prevent surface charging. The first electrode is at earth potential, the remaining voltage is applied to the second electrode, and the third electrode is maintained at the detector quadrupole axis potential. The distance from the crossing point to the third electrode is 69 mm and the angular resolution, which is defined by the third electrode, is approximately 3°. RPD analysers utilizing high transparency grids are not amenable to a theoretical treatment. However, the total resolution is estimated to be  $\Delta E \sim 0.04 E$  where  $E$  is the applied retarding potential. The largest contribution to the total resolution is due to the deviation of the potential between the grid wires from the applied potential.

### 3. DATA ACQUISITION

Product ion intensity contour diagrams are derived from measurements of the angular distributions of the production in the plane of the two beams and of their energy distributions at several angles. The neutral beam is chopped by a segmented disc, driven by a synchronous motor, at a frequency of 10–30 Hz and the background counts subtracted. There is no detectable background modulation. Energy distributions are recorded as a function of retarding potential in a multichannel analyser using 256 channel resolution. Data from the multichannel analyser are output on an X–Y recorder, smoothed manually and differentiated. Our data are presented on contour diagrams in cartesian co-ordinates [9] of intensity per unit velocity space volume normalized to unit beam strengths.

#### 4. PERFORMANCE

To assess the performance of the crossed beam apparatus we have measured the angular and energy distributions for elastic scattering and for charge exchanges in Ar-Ar collisions. This provides a very useful test, as the energy of the product ion varies over a wide range in a predictable way with angle enabling one to calibrate the energy scale and assess the performance of the detector without low velocity ions. When plotted on a contour diagram, as shown in figure 2, the velocity distributions follow the elastic circle indicating that no significant correction to the energy scale is required for contact potentials. The angular distributions have been transformed to centre of mass (CM) coordinates and compared with measured differential cross sections. We find good agreement with the results of Tsai *et al.* [10] except at wide angles where the

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$\text{Ar}^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{Ar}$   
Relative Energy = 2.50 eV

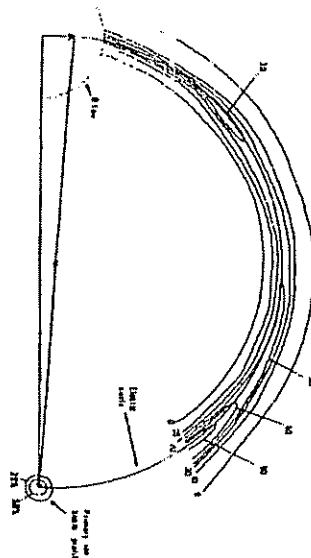
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Figure 2. Contour map of intensity of  $\text{Ar}^+$  from  $\text{Ar}^+ + \text{Ar}$  collision in centre of mass coordinate system for initial relative energy of 2.50 eV. Data with laboratory energy less than 0.1 eV are not included. Cross marks the centre of mass.

collection efficiency of the low velocity ions (laboratory energy less than 0.1 eV) is low. The rainbow angle in both the elastic scattering and charge transfer regions is in agreement with the results of Vestal *et al.* [10] within experimental error.

### 5. RESULTS AND DISCUSSION

The primary  $\text{CO}^+$  beam is produced with an ionizing electron beam of energy less than 35 eV. Electron impact on CO gives  $\text{CO}^+$  predominantly in the  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $B^1\Sigma^+$  states. The  $\text{CO}^+(B^1\Sigma^+)$  state has a lifetime of the order of  $5 \times 10^{-4}$  s [11] and radiates rapidly to the ground state. The  $A^1\Pi$  state is longer lived, but it can be estimated from the radiative lifetime (of the order of  $2-4 \times 10^{-4}$  s) [12] and the electron impact cross sections of the three states [13], that less than 1 per cent of  $\text{CO}^+(A^1\Pi)$  reaches the crossing region. Several workers [14, 15] have investigated the reaction



and suggested that a long lived electronic state of  $\text{CO}^+$ , possibly  $^4\Sigma$  (which has not been observed experimentally) is responsible. Ryan and Stone [15] have estimated that approximately 1 per cent of the  $\text{CO}^+$  produced by 30 eV electron impact is in the postulated  $^4\Sigma$  state. However, it seems unlikely that such small amounts of either the  $A^1\Pi$  or a metastable quartet state should be responsible for the intensities of product ions we observe under crossed beam conditions. We conclude, therefore, that the reactive species is  $\text{CO}^+(X^1\Sigma^+)$ .

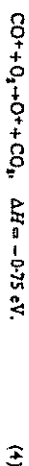
*Crossed beam study of  $\text{CO}^+ + \text{O}_2$*

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The  $\text{CO}^+(X^1\Sigma^+)$  produced by direct electron impact can be estimated from Franck-Condon factors to be predominantly in the  $v=0$  state. However, transitions from the  $B^1\Sigma^+$  and  $A^1\Pi$  states enhance the populations of higher vibrational levels. Moran *et al.* [16] have calculated the vibrational state distributions for a range of electron energies. At 30 eV, although the  $v=0$  level is predominantly populated (approximately 70 per cent), vibrational levels up to  $v=5$  have populations greater than 1 per cent. Since radiative vibrational de-excitation within a given electronic state appears to be slow in  $\text{CO}^+$  [17] there will be no significant relaxation in the time taken to travel to the crossing region.

Reaction (2) was studied at six energies over the initial relative kinetic energy range 1.8–10.1 eV. In addition to obtaining intensity contour diagrams for  $\text{CO}^+$ , we measured the angular distributions of the ion  $\text{C}^+$ ,  $\text{O}^+$  and  $\text{O}_2^+$  resulting from  $\text{CO}^+ - \text{O}_2$  collisions. Although the laboratory angular distributions cannot be related to the total cross section, some qualitative conclusions can be drawn.

The intensity of  $\text{O}^+$  is very low at low initial translational energies but rises between 3.6 and 5.0 eV and increases further as the relative translational energy is raised. At 10 eV the  $\text{O}^+$  intensity is significantly larger than the  $\text{CO}^+$  intensity. Since the rise in  $\text{O}^+$  intensity occurs in the range of initial relative energies where it becomes energetically possible for  $\text{CO}^+$  to dissociate, the  $\text{O}^+$  presumably arises from this rather than the exothermic reaction [6]



The  $\text{C}^+$  is present at very low intensity even at low initial translational energy and the intensity increases slightly as the energy is raised. Since channels for  $\text{C}^+$  formation are very endothermic it seems that a long lived excited electronic state of  $\text{CO}^+$  must be involved. The angular distribution of  $\text{O}_2^+$  is broad.

Relative cross-sections for the formation of  $\text{CO}^+$  have been obtained from the contour diagrams. The cross-section rises rapidly to a peak at initial relative energies around 5 eV and then decreases as an increasing amount of product  $\text{CO}^+$  is formed with internal excitation greater than the dissociation limit. A possible explanation for the variation of cross-section with energy is to suggest the existence of an avoided surface crossing. Collisions at low energy lead to charge transfer but as the energy is increased crossings to a surface leading to  $\text{CO}^+ + \text{O}$  become more probable.

Figures 3–5, 8, 9 present the relative intensity contour diagrams obtained at initial relative kinetic energies of 1.81, 2.78, 5.04, 7.49 and 10.12 eV. The translational exoergicity  $Q$ , defined as  $Q = T - T^*$  where  $T$  and  $T^*$  are the initial and final relative translational energies, has the limits  $-\Delta E \geq Q \geq -(D + \Delta E)$  where  $-\Delta E$  is the reaction exoergicity and  $D$  is the dissociation energy of the product ion. For reaction (2), assuming that the reactants are in their ground electronic and vibrational states and that the products are in ground electronic states,  $Q$  has the limits  $0.58 \geq Q \geq -4.72$  eV for dissociation into the lowest energy fragments  $\text{O}^+(^4\Sigma) + \text{CO}(^1\Sigma)$ . For dissociation into the next lowest energy channel,  $\text{CO}^+(X^1\Sigma^+) + \text{O}(^4P)$ , the limits for  $Q$  would be  $0.58 \geq Q \geq -5.10$  eV. The observed dissociation threshold is consistent with dissociation to  $\text{O}^+(^4\Sigma) + \text{CO}(^1\Sigma)$ . In all the contour diagrams measured no significant intensity lies outside the circle  $Q < 0.58$  eV. The contour diagrams over the whole energy range are asymmetric with respect to the  $\pm 90^\circ$  axis indicating that the reaction is



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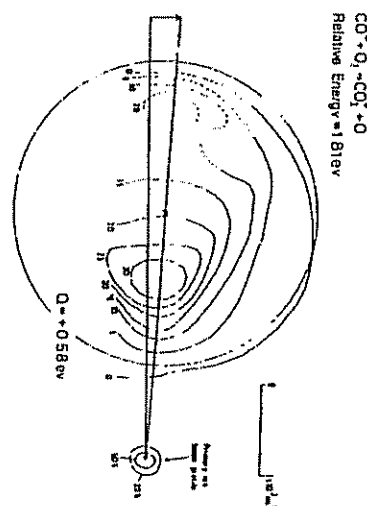


Figure 3. Contour map of intensity of  $\text{CO}_2^+$  in centre of mass coordinate system for initial relative kinetic energy of 1.81 eV. Contours mark the centre of mass and spectator stripping velocity.

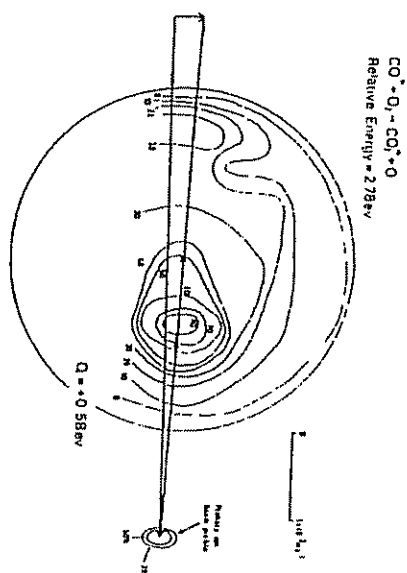


Figure 4. Contour map of intensity of  $\text{CO}_2^+$  for initial relative energy of 2.78 eV.

Ground beam study of  $\text{CO}^+ + \text{O}_2$ 

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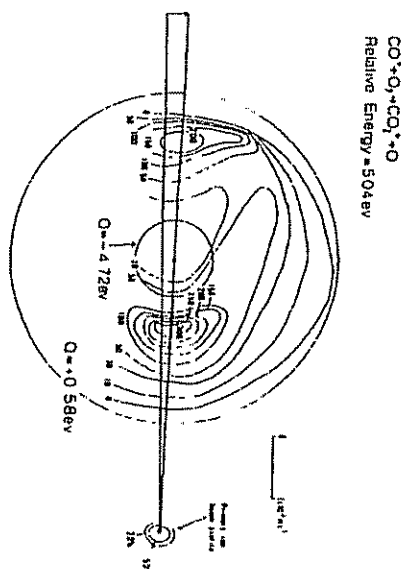


Figure 5. Contour map of intensity of  $\text{CO}_2^+$  for initial relative energy of 5.04 eV.

direct. This would be expected since  $\text{CO}_2^+$  is unlikely to have a potential well of any significant depth [18].

The contour diagram measured at the lowest relative translational energy  $T = 1.81$  eV (figure 3) shows a broad forward peak with a low intensity tail extending past the centre of mass and a smaller backward peak. There is a large uncertainty in the intensity of ( $\pm 50$  per cent) and position ( $\pm 20$  per cent) of the backward peak. Large uncertainties in the apparent intensities of low energy components is a well known problem with RPD analysers. The wide angular and velocity distribution suggests that at this energy the system passes through a region of the potential hypersurface in which all four atoms are strongly coupled. As the initial relative translational energy is raised to  $T = 2.78$  eV (figure 4) the forward peak becomes narrower and clearly lies at CM velocity lower than predicted by the spectator stripping model. As the energy is further raised to 5.04 eV (figure 5), the angular and velocity distributions of the forward peak become narrower as the mechanism becomes more impulsive. The backward peak increases relative to the forward peak as the energy is raised from 1.81 eV to 5.04 eV and lies at a CM velocity greater than the forward peak and outside the elastic stripping circle indicating that low impact parameter collisions in which all atoms strongly interact lead to product recoil and lower internal excitation than the grazing collisions which produce the forward peak.

A plot of translational exoergicity  $Q$  of the maximum of the forward peak against the initial relative translational energy  $T$  (figure 6) is a straight line over the energy range 1.81–5.04 eV. The internal excitation increases more rapidly than predicted by the spectator stripping model indicating the conversion of a

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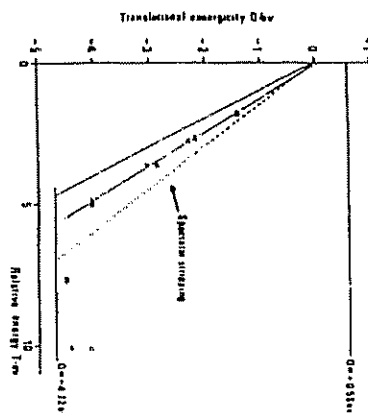


Figure 6. Plot of translational energy  $E_{tr}$  versus initial relative kinetic energy  $T_{rel}^i$ .

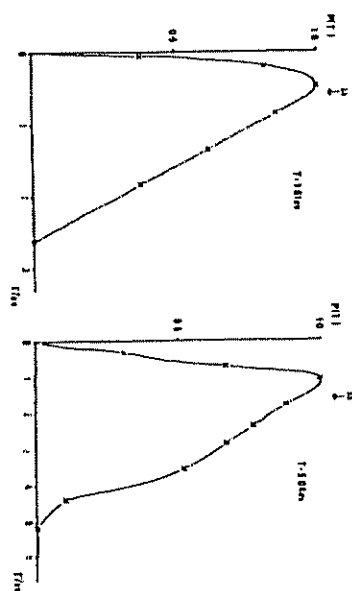


Figure 7. Distributions of relative translational energy of products,  $P(T^*)$  for initial relative energies of 1.81 and 5.04 eV.

constant fraction of the kinetic energy of the freed oxygen into internal energy of the product  $\text{CO}_2$ , showing that even in grazing collisions there is substantial interaction between all four atoms. The relative translational energy distribution of the products  $P(T)$  [20], derived from the contour diagrams, (figure 7) in this energy range show a similar trend.

Crossed beam study of  $\text{CO}^+ + \text{O}_2$ 

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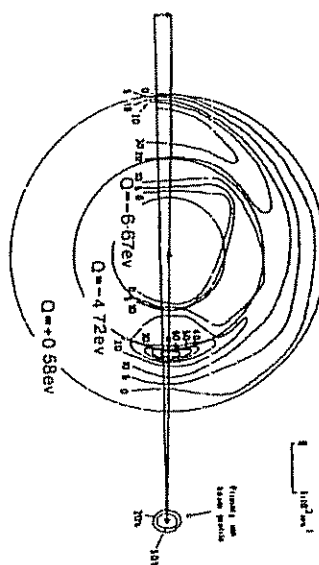
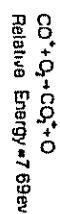


Figure 8. Contour map of intensity of  $\text{CO}_2^-$  for initial relative energy of 7.09 eV.

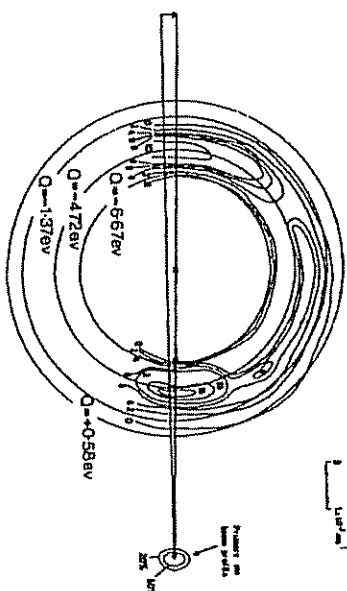
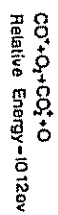


Figure 9. Contour map of intensity of  $\text{CO}_2^+$  for initial relative energy of 10-12 eV.

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As the energy is increased above 5 eV the total cross-section is observed to fall due to dynamic restrictions placed on product stability. The distribution of  $\text{CO}_2^+$  from  $\text{CO}^+-\text{O}_2$  collisions at an initial relative energy of 7.69 eV is shown in figure 9. The trend towards increased backward scattering continues and integrations to obtain the three-dimensional CM-angular distributions  $I(\chi)$  from

$$I(\chi) = \sin \chi \int_0^\pi \int_0^{2\pi} I_{\text{CM}}(\chi, \theta, \phi) d\theta d\phi, \quad (5)$$

show that the product is mainly backward scattered (figure 10). The maximum of the forward peak lies just outside the  $Q = -4.72$  eV circle. At this energy repulsive forces will dominate the kinematics. The spectator stripping point lies just within the  $Q = -4.72$  eV circle and strong interaction between the incipient  $\text{CO}_2^+$  and O is required to produce ground state products which are stable relative to dissociation. The increase in backward scattering shows that rebound or small impact parameter collisions in which all atoms interact strongly are more effective in producing stable product than grazing collisions.

As the initial relative translational energy is raised an increasing fraction of the product intensity is observed to fall within the circle  $Q = -4.72$  eV. There is however a dissociation threshold at  $Q \approx -4.72$  eV corresponding to dissociation to  $\text{O}^+(^4S) + \text{CO}(^1\Sigma^+)$  by a spin forbidden predissociation from the high vibrational level of the ground state. The C state of  $\text{CO}_2^+$  is known to be completely predissociated [19]. Since most of the intensity occurs at  $Q > -4.72$  eV, this implies that for the majority of the collisions the neutral product is  $\text{O}^+(^4P)$  and that all the internal excitation resides in the ionic product. For the product which lies within the  $Q = -4.72$  eV circle either O or  $\text{CO}_2^+$  must be electronically excited. The limiting values of  $Q$  for the formation of  $\text{O}^+(^4D)$  and  $\text{CO}_2^+(^2\Sigma^+)$  are

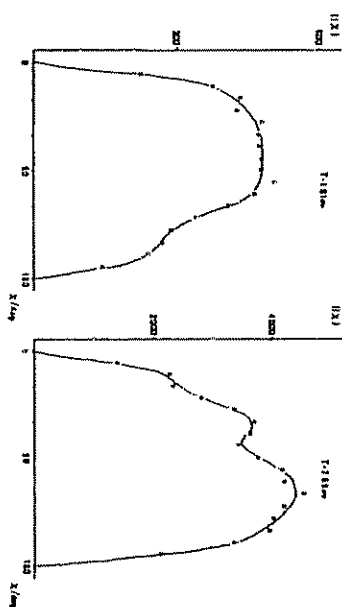


Figure 10. Centre of mass angular distributions of  $\text{CO}_2^+$ ,  $I(\chi)$  for initial relative energies of 1.81 and 7.69 eV.

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are  $-1.37$  eV  $\geq Q \geq -6.67$  eV and the contour diagrams are consistent with this, intensity within the circle  $Q = -6.67$  eV arises from the finite angular and energy resolution of the apparatus.

At the highest initial relative energy (10.12 eV) at which we performed an experiment the contour diagram (figure 9) shows a forward peak and a small maximum at  $\chi \sim 40^\circ$  just inside the  $Q = -4.72$  eV limit. The CM angular distributions show that there is an increase in wide angle scattering and that more intensity is scattered forwards than backwards. The backward peak lies within the stability limits for formation of the electronically excited products  $\text{CO}_2^+(^2\Pi_g) + \text{O}^+(^4D)$ . The spectator stripping point lies within the  $Q = -6.67$  eV circle though the forward peak is retained having shifted to a higher velocity. In H atom transfer reactions marked exoergicity is usually connected with a feature of the potential energy surface which allows product formed by grazing collisions to recoil directly forward. However reaction (2) is not very exoergic and recoil substantially in excess of that due to release of exoergicity is required to produce ground state forward scattered product. It is possible that the forward peak could arise from the reaction of the small component of electronically excited  $\text{CO}^+(^4\Sigma^-)$  in the ion beam. As we cannot vary the proportions of the excited states in the beam we cannot investigate this possibility. The increase in wide angle scattering and the small maximum at  $\chi \sim 40^\circ$  suggests that sequential impulses are becoming an important mechanism for product stabilization.

It should be noted that in addition to forming  $\text{CO}_2^+$  by the stripping of an oxygen atom from  $\text{O}_2$  by  $\text{CO}^+$  there is the possibility of forming  $\text{CO}_2^+$  by the stripping of C<sup>+</sup> by  $\text{O}_2$  to give  $\text{COO}^+$  followed by rearrangement, or by direct stripping of C<sup>+</sup> into the  $\text{O}_2$  bond. An assessment of the feasibility of such mechanisms would require reliable potential surfaces and detailed trajectory calculations. No conclusions can be drawn from the contour diagrams, though it should be possible to distinguish between these two mechanisms in future experiments using  $\text{C}^{18}\text{O}^+$ .

We gratefully acknowledge financial support and a studentship to (MFT) from the Science Research Council. We thank Shell Research Ltd. for providing the vacuum system and other equipment from which we developed the instrument. Our thanks are also due to Mr. C. Worland for machining services, and to members of the Warwick Mass Spectrometry Group and Dr. M. Levy for useful discussions.

## REFERENCES

- (1) HEDMAN, Z. and WOLFE, R., 1972, *Ion-Molecule Reactions*, Vol. 2, edited by J. L. Franklin (Butterworth & Co.), p. 563.
- (2) GENTY, W. R., 1979, *Gaz. Phys. Ion Chemistry*, Vol. 2, edited by M. T. Bowers (Academic Press), p. 221.
- (3) FERGUSON, F. C., SCHMELTZOFF, A. L. and FERGUSON, E. E., 1966, *J. Chem. Phys.*, 45, 21.
- (4) HEDMANN, R. S., BOLGER, R. C., SHAW, M. J. and TWIDY, N. D., 1970, *Chem. Phys. Lett.*, 5, 217.
- (5) ADAMS, N. G., SMITH, D. and GENTY, D., 1978, *Int. J. Mass Spectrom. Ion Phys.*, 26, 405.
- (6) BORTNER, M. H. and BARNER, J. (eds), 1972, *Reaction Rate Handbook*, 2nd edition (Defense Nuclear Agency).



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- [7] Katsurami, N., and Koyano, Y., 1974, *J. Phys. Soc. Japan*, **31**, 1082.
- [8] Barmann, K., Hurr, D. M., and Jaramid, M. F., 1978, *J. Phys. E*, **11**, 1037.
- [9] Wolcman, K., and Chao, R. J., Jr., 1969, *J. Phys. Chem.*, **73**, 743.
- [10] Varral, M. L., Blaker, C. R., and Furrer, J. H., 1978, *Phys. Rev. A*, **17**, 1337.
- [11] Jaramid, S. W., and Sorenson, G., 1975, *J. Chem. Phys.*, **62**, 2550.
- [12] Montanari, G. R., and de Hien, P. J., 1976, *Chem. Phys. Lett.*, **43**, 170.
- [13] Asari, J. F. M., and de Hien, P. J., 1970, *Physica (Utrecht)*, **49**, 435.
- [14] Chavaz, V., and Harnan, Z., 1965, *Collo. Czech. Chem. Commun.*, **30**, 1345.
- [15] Chavaz, V., and Harnan, Z., 1967, *J. Chem. Phys.*, **46**, 997.
- [16] Ryan, K. R., and Stock, H. M., 1976, *Int. J. Mass Spectrom. Ion Phys.*, **21**, 389.
- [17] Moberly, T. F., Wilcox, J. H., and Asari, L. E., 1978, *J. Chem. Phys.*, **68**, 261.
- [18] Moberly, T. F., and Friedman, L., 1965, *J. Chem. Phys.*, **42**, 2391.
- [19] Suck, L. W., and Gossard, R., 1974, *J. Res. Natl. Bur. Stand. A*, **78**, 315.
- [20] Elvén, J. H. D., 1972, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 371.
- [21] Harnan, Z., and Barmann, K., 1973, *Ber. Bunsenges. phys. Chem.*, **77**, 566.

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# Quantum collinear reaction probabilities for vibrationally excited reactants: $F + H_2(v \leq 2) \rightarrow FH(v \leq 5) + H$

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Quantum mechanical reaction probabilities are reported for the collinear reaction  $F + H_2(v) \rightarrow FH(v') + H$  in an energy range where two or three vibrational  $H_2$  states  $v$  are open. Rotated Morse-oscillator representations of the extended LEPS surfaces Muckerman *et al.* and *V*, and an adaptation of the BOP5 SCF-CI surface have been used. The scattering is dominated by resonances. A detailed investigation of the different kind of resonance behaviour is presented. For the two LEPS surfaces, overall features of the reaction probability curves can be correlated qualitatively in a one-to-one manner. Differences between the BOP5 and LEPS reaction probabilities are more pronounced for  $v=1$  than for  $v=0$ . For all surfaces, effects of vibrational excitation show a much more systematic behaviour in terms of the reverse reaction than for the forward reaction. A multi-step mechanism is deduced for the reaction, and an attempt is made to give an interpretation in terms of physical concepts including centrifugal effects, Franck-Condon transitions and quaground states. No obvious simple trends emerge from a statistical analysis. Most surprising plots are markedly non-linear in the energy range considered.

## 1. INTRODUCTION

An important topic in the theory of reactive molecular collisions is the effect on the scattering of variations in the potential energy surface. In a previous paper [1], we have reported accurate quantum results for the collinear exoergic reaction



with  $H_2$  in its vibrational ground state. Three different potential surfaces were used: the extended LEPS Muckerman *et al.* [2] and Muckerman *V* (M $V$ ) [3] surfaces, and an adaptation of the *ab initio* SCF-CI surface of Bender *et al.* (BOP5) [4]. The purpose of this paper is to report quantum reaction probabilities for the collinear reaction (1) in which  $H_2$  is vibrationally excited, with  $v=1$  or 2. The same three potential surfaces are again employed. For the M $V$  surface we compare our results with those of Schatz, Bowman and Kupperman [5, 6] (hereafter abbreviated SBK).

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## COUPLING A QUADRUPOLE MASS SPECTROMETER AND A FOURIER TRANSFORM MASS SPECTROMETER

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### ABSTRACT

Experiments performed by the authors during the last year have demonstrated the feasibility of a new analytical instrument called a tandem quadrupole-Fourier transform mass spectrometer (QFT-MS). Ions made in the source of a quadrupole mass spectrometer are extracted and focused into a beam. The ion beam is then injected axially into a superconducting electromagnet where the ions are stored in an analyzer cell and detected by Fourier transform mass spectrometry (FT-MS).

The goal of this project is to combine the highly developed chromatographic and sample ionization features of a quadrupole mass spectrometer with the versatility and high mass resolution that is available with Fourier transform detection. High mass resolution is possible because differential pumping separates the ion source of the quadrupole mass spectrometer from the analyzer cell of the FT-MS instrument. A novel method is described for efficiently injecting ions axially into the solenoidal magnetic field.

The QFT-MS instrument has many features in common with triple quadrupole mass spectrometers but with QFT-MS, much higher mass resolution is possible. For example, a mass resolution of 140000 is demonstrated for  $m/z$  78 ions produced by collision-induced dissociation of bromobenzene molecular ions.

### INTRODUCTION

Fourier transform mass spectrometry (FT-MS) utilizes advanced electronic techniques to achieve unmatched stability and mass resolution [1-4]. The operating principles of FT-MS are quite different from conventional quadrupole and sector mass spectrometers. There are no slits, flight tubes, high voltage power supplies, or electron multipliers needed. Instead, ions are trapped in an analyzer cell by a strong magnetic field and are detected by the image current induced by their cyclotron motion [5,6]. Two important features of FT-MS are that weak ion currents can be integrated for several seconds in the analyzer cell, and all ions can be detected simultaneously. In addition, a series of experiments, such as collision-induced dissociation and

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laser photodissociation, can be performed on the *same* set of ions while they are stored in the analyzer cell [7-10]. Mass spectrometry experiments involving pulsed lasers can be readily performed by FT-MS because all ions formed by the laser are trapped in the analyzer cell and a complete mass spectrum can be obtained for each laser pulse [11-13].

In spite of the many advantageous features of FT-MS, it has not been widely accepted for analytical applications. One difficulty is that the mass resolution and detection sensitivity of the spectrometer decrease severely at pressures exceeding about  $10^{-6}$  Torr. Thus, a mass resolution of  $M/\Delta M$  500 000 at a pressure of  $1 \times 10^{-8}$  Torr decreases to just  $M/\Delta M$  1000 at  $5 \times 10^{-6}$  Torr. This makes it difficult to interface an FT-MS instrument to previously developed separation and ionization techniques, such as fast atom bombardment (FAB), gas chromatography (GC) and liquid chromatography (LC), because all of these present a large gas load to the mass spectrometer. Another problem is that the analyzer cell does not work properly if the ion density exceeds about  $10^6$  ions  $\text{cm}^{-3}$ . An excessive number of ions in the analyzer cell causes the cyclotron resonance signals to become distorted and makes it difficult to detect minor components in the presence of abundant ions at another mass [14-16].

In 1982, we began working on a new approach to overcome these limitations of conventional FT-MS instruments. It involves coupling a quadrupole mass spectrometer and a Fourier transform mass spectrometer so that the ion production region is separated from the ion detection region. Ions are formed in the source region of a quadrupole mass spectrometer and are injected into a Fourier transform mass spectrometer where they are trapped and detected. This idea arose from the realization that FT-MS is a versatile and sensitive means for detecting ions, but an alternative means was needed for producing the ions and handling the high gas loads associated with coupling a GC or LC to the mass spectrometer.

In this paper, we describe a "tandem quadrupole-Fourier transform mass spectrometer" (QFT-MS) that was built during the last year and has been operational for about six months. A novel means for guiding the ion beam from the quadrupole mass spectrometer to the FT-MS analyzer cell is described and recent results showing high mass resolution and injection efficiency are presented.

#### EXPERIMENTAL

Figure 1 illustrates the concept of QFT-MS. Ions extracted from an ion source are injected into a first set of quadrupole rods (Q1) which can be operated in the rf-only or the rf/dc mode to transmit ions in a selected region of the mass spectrum. It functions as a handpass filter having a

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variable high mass and low mass cutoff. Unwanted ions are rejected by Q1 while the ions of interest are transmitted

Next, the ion beam enters a second quadrupole mass filter (Q2) which is normally operated in the rf-only mode. The purpose of Q2 is to guide the ion beam through the intense fringing fields of the superconducting magnet. As the ions enter the homogeneous region of the magnetic field, they are decelerated and trapped in the FT-MS analyzer cell. Several methods have been used to decelerate the ions. A description and comparison of these will be presented in a separate paper when more definitive data have been obtained. Once the ions are trapped in the analyzer cell, FT-MS detection can be performed in the conventional manner.

In January 1983, construction of a prototype QFT-MS instrument began with the assistance of engineers from the Finnigan Corporation [17]. The instrument has been modified extensively since then. Presently, it consists of a model 4500 ion source and vacuum manifold made by Finnigan MAT (355 River Oaks Parkway, San Jose, CA). The source is evacuated by a turbomolecular pump and liquid nitrogen trap. The guiding quadrupole Q2, which was designed specially for this project, is constructed of stainless steel rods held in place by ceramic spacers. An elongated trapped ion analyzer cell having dimensions  $8.9 \times 3.8 \times 3.8$  cm is used to store the ions and detect them by FT-MS [18]. The cryomagnet was made by Oxford Instruments (Osney Mead, Oxford, Gt. Britain). It has a room temperature bore diameter of 15 cm and can be energized to a peak field strength of 7 T. The manifold containing the analyzer cell is pumped by a closed-loop liquid helium cryopump to a base pressure in the mid- $10^{-9}$  Torr range. A pressure gradient of 120 was measured between the source housing and the analyzer cell. The electronics and computer data system developed for FT-MS

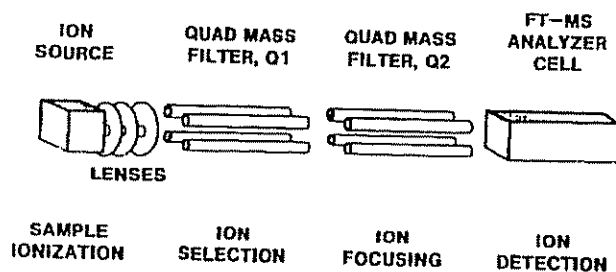


Fig. 1 Concept of QFT-MS. Ions produced by a quadrupole mass spectrometer are guided by a second quadrupole mass filter to an FT-MS analyzer cell where they are detected

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detection are now available as a commercial product from the IonSpec company (1 Longstreet, Irvine, CA).

The guiding quadrupole mass filter, Q2, is a key feature of this design because, without it, few ions would be able to pass to the FT-MS analyzer cell. The magnetic mirror principle, which is utilized in plasma physics for the containment of ionized gases, predicts that ions leaving the source of the quadrupole mass spectrometer (at a magnetic field strength of about 0.02 T) will be decelerated and reflected backwards as they approach the strong magnetic field (7 T) around the analyzer cell [19]. However, Q2 operated in the rf-only mode overcomes this problem because it focuses the ion beam and directs it precisely down the axis of the solenoidal magnet. The ions are not significantly decelerated by the magnetic mirror effect because they do not encounter the off-axis magnetic lines of force. We have modeled and studied the trajectories of ions in quadrupolar electric fields and inhomogeneous magnetic fields. The results of these calculations will be presented in a separate publication [20].

#### RESULTS AND DISCUSSION

An important goal for the QFT-MS instrument is to combine the best features of FT-MS and quadrupole mass spectrometry. Thus, the existing sample separation and ionization methods developed for quadrupole mass spectrometers could be utilized along with the high mass resolution available with FT-MS. With a properly designed vacuum manifold, the same GC and LC interfaces and FAB guns that are currently available on quadrupole mass spectrometers could be used with the QFT-MS. As improved interfaces are developed, they too could be readily adapted to the QFT-MS instrument because ample space is available in the region around the ion source. This is a cost effective approach because it eliminates the need to develop new types of interfaces suitable for the low pressure requirements of FT-MS.

All of these goals have not been realized with the prototype instrument, but the feasibility of injecting ions into the analyzer cell and detecting them at high mass resolution has been proven. The next six figures illustrate the level of performance achieved thus far with the prototype instrument.

Figure 2 is a plot of the ion current that reaches the FT-MS analyzer cell as the potential on a collector plate is varied. Both Q1 and Q2 were operated in the rf-only mode. The lower trace shows a maximum ion current of 280 pA when the FT-MS analyzer cell is withdrawn from the magnet by 2 m, while the upper trace shows that a much larger ion current, 1020 pA, is recorded, when the spectrometer is returned to its normal position where the FT-MS analyzer cell is in a field strength of 4.1 T. These results are opposite from what was expected. Apparently, Q2 is very effective in focusing the ion